CHARACTERIZATION AND TRANSFORMATION OF DISSOLVED ORGANIC MATTER USING ULTRA-HIGH RESOLUTION MASS SPECTROMETRY

A. Jaggi[1], J. Radovic[1], R. Silva[1], R. Snowdon[1], M. Brown[1], S. Larter[1], T. Oldenburg[1]

[1]University of Calgary, Calgary, Canada

Introduction

Dissolved organic matter (DOM) is considered an ultimate chemical product of a large variety of recent biological and fossilized organic matter. Being one of the largest active carbon pools on Earth, DOM integrates energy, carbon dioxide and nutrients into a vast compositionally and structurally diverse moiety of molecules that are further modified by physical, chemical and biological processes. As one of the largest reservoirs of reduced carbon on earth's surface, DOM plays a fundamental role in the global carbon cycle. In order to decipher the information that DOM holds, water samples were collected from varying depths and environmentally distinct geographical locations ranging from the pristine Arctic waters to the oil spill affected waters in the northern and southern Gulf of Mexico. The DOM extracted from these samples was then analysed using an ultra-high resolution 12T Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) using an APPI source in positive ion mode and an ESI source in negative ion mode.

Results

The DOM analysed using both the APPI and ESI sources, showed a remarkable similarity in the type of compound classes (a class is defined here as the sum of all constituents containing the same heteroatoms (number and elements) independent of the degree of unsaturation) present, despite the variability in the environmental conditions of the sampled sites. This similarity might suggest that the transformative processes (like microbial degradation, photo oxidation, abiotic, etc.) undergone by dissolved organics, irrespective of the nature of their source of input, ultimately lead to similar structural features. Within the compound class distributions, the multioxygenated constituents offered the highest contribution to the relative intensity of all compound classes present in the DOM. This is in agreement with previous studies, where the $C_cH_hO_o$ compounds were predominant in the DOM analysed using an ESI negative ion source (Koch *et al.*, 2007, Sleighter and Hatcher, 2008).

The DOM spectra analysed in ESI negative ion mode showed an increase in both the relative intensity and number of oxygen atoms in the O_x compound class from surface to bottom of the water column at the sampled sites. This change in the composition of the O_x compound classes from the surface towards the bottom might suggest either different biological processes at play, or an aging effect, i.e. slow settling of DOM over thousands of years towards the bottom of the ocean indicates that degree of oxygenation is a function of time. In either situation, it may provide insight into better understanding the nutrient and DOM cycling in the ocean.

The nitrogen containing compound classes showed the most variability between the geographically distinct, northern, and southern Gulf of Mexico and Arctic water DOM. The N/C ratio for the surface samples when divided by the corresponding ratio for the bottom samples, showed a difference of 0.10 between the northern and southern Gulf waters and of 0.20 between the northern Gulf and Arctic waters. These differences might suggest either different source input from the marine biosphere and possible terrestrial sources or different

transformation processes like biodegradation, photo oxidation and/or abiotic processes lead to the compositional variations.

Conclusions

This comprehensive study of DOM from geographically distinct waters might provide valuable insights into the origin of parent organic matter, biogenic and abiogenic inputs, and alteration processes. This information when decoded may help to better understand the carbon cycle and oceans as a CO_2 sink.

References

- Koch, B.P., Dittmar, T., Witt, M. and Kattner, G., 2007. Fundamentals of molecular formula assignment to ultrahigh resolution mass data of natural organic matter. *Analytical Chemistry*, *79*(4), pp.1758-1763.

- Sleighter, R.L. and Hatcher, P.G., 2008. Molecular characterization of dissolved organic matter (DOM) along a river to ocean transect of the lower Chesapeake Bay by ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Marine chemistry*, *110*(3), pp.140-152.